TRANSLATION

(54) [Title of the Invention]

Production Method for Modified Poly Ethylenic Resin, Modified Poly Ethylenic Resin and the Film Made From This Resin

(57) [Summary]

[Objective]

To offer the poly ethylenic resin which can be used to produce "inflation film" (*tubular blown film, Translator*) with an excellent balance of physical properties such as good

impact resistance and a low deviation in the film thickness.

[Method to Achieve the Objective]

The poly ethylenic resin obtained by using a Ziegler type catalyst and of which the density is 940 ~ 970 kg / m^3, the MFR (at a temperature of 190 °C and a load of 49 N) is 0.01 ~ 50 g / 10 min, and of which the tan δ at a temperature of 190 °C and an angular frequency of 1.5 x 10^{-2} rad / sec is 1.0 ~ 3.0, is introduced into the extruder after polymerization without practically contacting with air, and it is contacted with an oxygen- containing gas in this system, and thereafter, it is melt-kneaded, and by this, the tan δ of the resin is increased, and thus the modified poly ethylenic resin is produced.

[Scope of the Patent Application]

[Claim 1]

Method to produce modified poly ethylenic resin characterized by the fact that the poly ethylenic resin obtained by using a Ziegler type catalyst and of which the density is 940 ~ 970 kg / m^3, the melt flow rate (at a temperature of 190 °C and a load of 49 N) is 0.01 ~ 50 g / 10 min, and of which the tan δ at a temperature of 190 °C and an angular frequency of 1.5 x 10^{-2} rad / sec is 1.0 ~ 3.0, is introduced into the extruder after polymerization without practically contacting with air, and it is contacted with an oxygen-containing gas in this system, and thereafter, it is melt-kneaded, and by this, the tan δ of the resin is increased.

[Claim 2]

Method to produce the modified poly ethylenic resin in which the tan δ is increased by 1 ~ 150 % by melt- kneading, as was described in Claim 1.

[Claim 3]

Method to produce modified poly ethylenic resin in which the oxygen- containing gas that is contacted with the poly ethylenic resin in the extruder is such that the oxygen content is 0.5 ~ 50 volume %, as was described in Claim 1 or Claim 2.

[Claim 4]

Method to produce modified poly ethylenic resin in which an oxidation preventor is added at a concentration of 4000 ppm or less before the poly ethylenic resin melts, as was described in Claims 1, 2 or 3.

[Claim 5]

Method to produce the modified poly ethylenic resin in which the extruder is a biaxial screw extruder as was described in any one of Claims 1 to 4.

[Claim 6]

Method to produce the modified poly ethylenic resin in which the α-olefin units contained in the poly ethylenic resin before contacting it with the oxygen- containing- gas, are such that the number of carbon atoms is 3 to 20, and the content is 2 mole % or less, as was described in any one of Claims 1 to 5.

[Claim 7]

Method to produce modified poly ethylenic resin in which the poly ethylenic resin is produced by a continuous multi- stage polymerization with 2 or more stages, and the earlier stage produces the poly ethylene (A) of which the melt flow rate (at a temperature of 190 $^{\circ}$C and a load of 21.18 N) is 40 to 2000 g /10 min, and the density is 930 to 985 kg / m^3, and then the later stage produces the poly ethylene (B) in the presence of the said poly ethylene (A), and the proportion of poly ethylene (A) and poly ethylene (B) is adjusted to be in the range of 30 : 70 ~ 70 : 30 as the weight ratio, as was described in any one of Claims 1 to 6.

[Claim 8]

Method to produce modified poly ethylenic resin in which poly ethylene (A) is the ethylene homo polymer as was described in Claim 7.

[Claim 9]

Method to produce modified poly ethylenic resin in which poly ethylene (B) is a

co-polymer of ethylene and an α-olefin with 3 to 20 carbon atoms, as was described in Claim 7 or Claim 8.

[Claim 10]

Modified poly ethylenic resin characterized by the fact that it is obtained by the method described in any one of Claims 1 to 9.

[Claim 11]

Inflation film that uses the modified poly ethylenic resin described in Claim 10 as the base material.

[Detailed Explanation of the Invention]

[0001]

[Technical Field in Which this Invention Belongs]

This invention relates to the method to produce modified poly ethylenic resin, the modified poly ethylenic resin and the film made from this resin. In particular, it relates to the method to efficiently produce the modified poly ethylenic resin that can be used to produce inflation film with an excellent balance of physical properties such as good impact resistance and a low deviation in the thickness, etc., and also it relates to the modified poly ethylenic resin with the above mentioned characteristics obtained by this method, and the inflation film with an excellent balance of the physical properties which uses this modified poly ethylenic resin as the base material.

[0002]

[Existing Technology]

Poly ethylenic resin has been widely used in various fields as the general use resin, and one of the representative usages is for film. Among these resins, especially high density poly ethylene can form an inflation film with a thin film thickness, and also that film has excellent mechanical strength, therefore, it is suitable to be used for packaging usages. This inflation forming method is the method in which the melted high density poly ethylene is extruded in a ring shape from a ring shaped die, and it is continuously wound

up by solidifying it via air cooling while expanding it via inner pressure. In such inflation forming, in order to secure high productivity, even higher speed has been desired. However, when the forming is performed at high speed, the film is broken by the drawing, and also so- called spiral marks occur which are caused by the spiral flow of the melted resin inside the die appearing on the flow from the die slip (*this was phonetically written and looks like a typo of 'slit', Translator*) exit "as is", and a uniform thickness of the film can not be maintained. As a result, wrinkles or slats will occur on the film, and this affects the secondary work processing of the film such as printing ability, or slitability, and product failures can occur, or a snake-like movement of the film can occur in the bag making process and problems such as a decrease in the speed of bag making or failures of heat sealing can occur. On the other hand, in order to maintain the uniform thickness of the film, the productivity of the film making had to be decreased.

[0003]

In order to solve the problems like these, until now, various counter measures have been tried from the form working stand point such as; a rotary die is used, the bubble cooling was made more efficient by an internal cooling system, the die slip? was made narrower, etc., however, all of these can not sufficiently obtain satisfactory physical properties of the film. Also, the method in which a radical initiator or a cross linking agent is added during the kneading time to obtain the film forming material, has been suggested (Patent Application Kokai No. S60-161131). However, in this method, the impact strength of the film decreases although the thickness unevenness can be decreased, and also gel formation occurs during the inflation film forming time, and the appearance of the film deteriorates, and these are not preferred. On the other hand, Patent Application Kokai No. H7-276495 showed an example in which the relationship between the distortion curing parameter and the thickness unevenness was investigated. However, according to a study done by the inventors of this invention, the high speed forming ability was not satisfactory, although the thickness unevenness is less. In addition, the method of modifying the poly ethylene resin produced using a chromium type catalyst has been suggested too (Patent Application Kokai No. H8-90633). However, in this modifying method, high molecular weight poly ethylene is formed by a cross linking reaction, and as

the result, the viscosity of the poly ethylene increases, therefore the amount discharged during the inflation forming time decreases, and the motor load increases, and in addition, fish eyes occur on the film due to the formation of high molecular weight components, and this greatly deteriorates the quality of the film. On the other hand, in order to make the thickness even, the technique in which the poly ethylene is granulated under the conditions of a specific oxygen concentration has been suggested (Patent Application Kokai No. H11-71427). However, in this technique, gel appears in the film and it is not satisfactory.

[0004]

[Problem That this Invention Intends to Solve]
The objective of this invention is to offer the poly ethylenic resin with which the bubble stability is good during the inflation forming time, and which can be used to produce the inflation film with an excellent balance of physical properties such as good impact resistance and a low deviation in the thickness, and which has fewer fish eyes, and also to offer the inflation film with an excellent balance of physical properties that uses this resin as the base material.

[0005]

[Method to Solve the Problem]
To achieve the above mentioned objective, the inventors investigated, and as the result, they discovered that the modified poly ethylenic resin that was obtained by introducing the poly ethylenic resin that was obtained by using a Ziegler type catalyst and that has a specific nature, into the extruder without contacting it with air practically after polymerization, and by contacting it with an oxygen- containing gas in this system, and thereafter by melt- kneading it, can meet this objective. This invention was made based on this discovery.

[0006]

Namely, this invention offers the method to produce the modified poly ethylenic resin characterized by the fact that poly ethylenic resin obtained by using a Ziegler type catalyst

and of which the density is 940 ~ 970 kg / m^3, the melt flow rate (at a temperature of 190 °C and a load of 49 N) is 0.01 ~ 50 g / 10 min, and of which the tan δ at a temperature of 190 °C and an angular frequency of 1.5 x 10^{-2} rad / sec is 1.0 ~ 3.0, is introduced into the extruder after polymerization without practically contacting it with air, and it is contacted with an oxygen- containing gas in this system, and thereafter, it is melt-kneaded, and by this, the tan δ of the resin is increased. Also, this invention offers the modified poly ethylenic resin obtained by the above mentioned method, and the inflation film that uses this modified poly ethylenic resin as the base material.

[0007]

[Form to Bring this Invention into Practice]

In the production method for modified poly ethylenic resin of this invention, the poly ethylenic resin to be used for modification is the one that is obtained by using a Ziegler type catalyst. Namely, those where ethylene, or ethylene and an α -olefin are polymerized in presence of a Ziegler type catalyst that includes a transition metal component such as titanium and an organic aluminum compound, are used. To be concrete, it is preferred to use a so called supported type Ziegler catalyst of which the main components are the solid catalytic component that includes magnesium, titanium, a halogen, and an organic aluminum compound. As the polymerization method, the solution polymerization method, the slurry polymerization method, the gas phase polymerization method, etc., can be used. In solution polymerization or slurry polymerization, an inert hydrocarbon may be used as the solvent, or the olefin itself may be used as the solvent. Concerning the inert hydrocarbon solvent, to be concrete, aliphatic hydrocarbons such as butane, iso butane, pentane, hexane, octane, decane, dodecane, hexa decane, octa decane, etc.; alicyclic hydrocarbons such as cyclo pentane, methyl cyclo pentane, cyclo hexane, cyclo octane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; petroleum fractions such as gasoline, kerosene, light oil, etc.; can be listed. Among these inert hydrocarbon solvents, the aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions are preferred.

[0008]

In this invention, the resin that has the following nature is used as the poly ethylenic resin. First, the density should be in the range of 940 to 970 kg / m^3. If the density is less than 940 kg / m^3, the rigidity is insufficient. and if it exceeds 970 kg / m^3, the impact strength decreases. Considering the rigidity and impact resistance, the preferred density should be in the range of 945 to 965 kg / m^3, and 945 to 960 kg / m^3 is more preferred. Also, the melt flow rate (MFR) measured at 190 $^{\circ}$C with a load of 49 N, should be in the range of 0.01 to 50 g / 10 min. If this MFR is less than 0.01 g / 10 min, it lacks fluidity so that the forming ability is extremely poor, and if it exceeds 50 g / 10 min, the impact strength decreases. Considering the forming ability and the impact resistance, the preferred MFR should be in the range of 0.05 to 10 g / 10 min, and the range of 0.10 to 1 g / 10 min is especially preferred. Also, the tan δ at a temperature of 190 $^{\circ}$C and an angular frequency of 1.5 x 10^{-2} rad / sec should be in the range of 1.0 ~ 3.0. If this tan δ is outside the above mentioned range, the objective of this invention can not be achieved. The preferred tan δ should be in the range of 1.1 to 2.5, and the range of 1.2 to 2.0 is especially preferred. The methods used to measure these physical properties will be explained later.

[0009]

The poly ethylenic resin used in this invention may be a homo polymer too, but the poly ethylenic resin that is comprised of at least two kinds of poly ethylenes, (A) and (B), is preferred. In this case, poly ethylene (A) and poly ethylene (B) must be uniformly mixed. Therefore, it is preferred to produce the poly ethylenic resin by the method in which the poly ethylenes (A) and (B) that were produced beforehand are dry blended, and thereafter this mixture is melt- kneaded sufficiently. In the case when the poly ethylenes (A) and (B) are dry blended as pellets, it will not be mixed uniformly, and not only can the bubble stability not be secured during the film forming time, but also a large amount of fish eyes might occur on the film. As another method to mix these sufficiently uniformly, the production method of a multi- stage continuous polymerization with 2 or more stages can be used preferably too. In this case, the earlier stage produces poly ethylene (A) and the later stage produces poly ethylene (B) preferably.

[0010]

The MFR of the above mentioned poly ethylene (A) measured at 190 °C with a load of 21.18 N, should be normally 40 to 2000 g / 10 min, preferably 50 to 1500 g / 10 min, and more preferably 100 to 1100 g / 10 min. (*the following words look like a typo, but they probably mean; "If the MFR is less than 40 g / 10 min", Translator*), the fluidity might decrease, and if it exceeds 2000 g / 10 min, not only does junk appears around the vicinity of the extruder die, but also the film strength decreases, and fish eyes sometimes appear on the film. The density of poly ethylene (A) should be normally 930 to 985 kg / m^3, preferably 950 to 985 kg / m^3, and more preferably it should be 960 to 985 kg / m^3. If this density is less than 930 kg / m^3, the rigidity of the film might decrease. This poly ethylene (A) should be preferably a homo polymer of ethylene.

[0011]

On the other hand, poly ethylene (B) can be a homo polymer of ethylene or a co-polymer, but preferably it should be the co-polymer of ethylene and an α -olefin. As this α -olefin, the ones with 3 to 20 carbon atoms are preferred, and especially the ones with 4 to 10 carbon atoms are preferred. As such α -olefins, for instance, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1- decene, etc., can be listed. More preferably, 1-butene can be listed. The proportion of polyethylene (A) and poly ethylene (B) should be preferably 30 : 70 ~ 70 : 30 as the weight ratio, and more preferably 40 : 60 ~ 60 : 40, and even more preferably it should be 50 : 50 ~ 60 : 40. Based on the total amount of poly ethylene (A) and poly ethylene (B), if the poly ethylene (A) content is less than 30 wt %, it lacks fluidity, and when it exceeds 70 wt %, fish eyes might occur in the film.

[0012]

In the method of this invention, the above mentioned poly ethylenic resin produced by using a Ziegler type catalyst is dried in the system, and thereafter it is introduced into the extruder without practically contacting it with air, and it is contacted with an oxygen-containing gas in the extruder. The reason for this is because the poly ethylenic resin produced by using a Ziegler type catalyst is in powder form so that it has a large surface

area, and it can be easily de-natured by contacting it with air. In this invention, after the poly ethylenic resin is contacted with an oxygen- containing gas in the extruder, it is melt-kneaded to increase the above mentioned tan δ. At this time, the said tan δ should be increased 1 to 150 %, preferably 1 to 100 %, and a 5 to 80 % increase is more advantageous. If the increase in this tan δ is less than 1 %, the effect of improvement (modifying effect) will not be exhibited sufficiently. If it exceeds 150 %, the obtained modified poly ethylenic resin becomes yellowish, and the impact resistance sometimes decreases. The temperature for extruding the resin should be preferably in the range of 200 to 330 $^\circ$C.

[0013]

Concerning the extruder, one which has twin axis screws such as a same rotational direction biaxial extruder, a different rotationl direction biaxial extruder, etc., are preferred. TEX, CMP-X, CMP-XII made by Nihon Seiko K.K., TEM made by Toshiba Kikai K.K., KTX made by Kobe Seiko K.K. and SZK made by KRUPP WERNER & PFLEIDERER can be listed as the same rotational direction biaxial extruders, and CIM, CIM-P, CIM-PII made by Nihon Seiko K.K., FCM, LCM-G and LCM-H, etc., made by Kobe Seiko K.K., can be listed as the different rotational direction biaxial extruders. Also, a tandem extruder which is the combination of more than one of these extruders (including the one where the second stage is a single axis extruder) can be used too.

[0014]

Concerning contact with the oxygen- containing gas, the effect will be exhibited at any area of; the hopper of the extruder, the hopper chute, the solid transport part and the plasticizing part. In addition, even in the case where contact occurs in the feeder to the extruder, if the oxygen- containing gas accompanies the material to the extruder, a similar effect can be exhibited. In this region, the resin is a powder, therefore we think the oxygen- containing gas contacts with the resin more evenly. Therefore, the preferred place is the hopper of the extruder, the hopper chute, and the solid transport part. In order to efficiently transport the poly ethylene resin powder in the solid transport part and to mix the poly ethylenic resin very uniformly, the bulk density of this powder should be

0.2 to 0.6 g / cm^3, and preferably it should be 0.3 to 0.4 g / cm^3. The specific energy used during the kneading time should be preferably 0.05 to 0.5 kW X h / kg, and more preferably it should be 0.07 to 0.4 kW X h / kg.

[0015]

The oxygen concentration in the oxygen- containing gas should be normally 0.5 to 50 vol. %, preferably 1 to 21 vol % and more preferably it should be 1 to 5 vol %. If this oxygen content is less than 0.5 vol %, the effect of bubble stabilization is sometimes not sufficient, and when it exceeds 50 vol %, the obtained modified poly ethylenic resin becomes yellowish, and also, the safety during the production sometimes can not be secured. The oxygen content can be adjusted while measuring it using a device that utilizes electric conductivity or by using gas phase chromatography. For instance, in the case when the mixed gas that contains oxygen is contacted with the poly ethylenic resin in the hopper, the sensor of the measuring device should be installed inside the hopper or the lower part near the entrance to the solid transport part of the extruder. Also, before the poly ethylenic resin is melted, if desired, an oxidation preventor may be added appropriately at 4000 ppm or less, preferably 3000 ppm or less, more preferably at 2000 ppm or less. This is because, depending on the resin, in some cases, even though the modification method of this invention is used, tan δ of the poly ethylenic resin does not increase, and the objective of this invention can not be achieved sufficiently, and the poly ethylene resin sometimes becomes yellow.

[0016]

As this oxidation preventor, for instance, phenolic stabilizers, organic phosphite type stabilizers, thio ether type stabilizers, hindered amine type stabilizers, etc., can be used. As the phenolic stabilizers, for instance, 2, 6- di-t-butyl -4- methyl phenol; 2, 6-di-t- butyl -4- ethyl phenol; 2, 6- di- cyclo hexyl -4- methyl phenol; 2, 6- di- iso propyl -4- ethyl phenol; 2, 6- di- t- amyl -4- methyl phenol; 2, 6- di-t- octyl -4- n-propyl phenol; 2, 6- di- cyclo hexyl -4- n- octyl phenol; 2- iso propyl -4- methyl -6- t- butyl phenol; 2-t- butyl -2- ethyl -6- t- octyl phenol; 2- iso butyl -4- ethyl -5- t- hexyl phenol; 2- cyclo hexyl -4- n- butyl -6- iso propyl phenol; styrenated mixed cresol; dl- α - tocopherol; t- butyl hydroquinone;

2, 2'- methylene bis (4- methyl -6-t- butyl phenol); 4, 4'- butylidene bis (3- methyl -6-t-butyl phenol); 4, 4'- thio bis (3- methyl -6- t- butyl phenol); 2, 2'- thio bis (4- methyl -6- t-butyl phenol); 4, 4'- methylene bis (2, 6- di-t- butyl phenol); 2, 2'-methylene bis [6- (1-methyl cyclo hexyl) -p- cresol]; 2, 2'- ethylidene bis (4,6- di-t- butyl phenol); 2, 2'-butylidene bis (2-t- butyl -4- methyl phenol); 1, 1, 3- tris (2- methyl-4- hydroxy -5-t- butyl phenyl) butane; tri ethylene glycol - bis [3-(3-t-butyl -5- methyl-4- hydroxy phenyl) propionate]; 1, 6- hexane diol -bis [3-(3, 5- di- t- butyl -4- hydroxy phenyl) propionate]; 2, 2'- thio di ethylene bis [3- (3, 5-di- hydroxy t- butyl -4- hydroxy phenyl) propionate; N, N'- hexa methylene bis (3, 5-di-t- butyl -4- hydroxy - hydro cinnamide); 3, 5- di-t- butyl -4-hydroxy benzyl phosphonate - di ethyl ester; 1, 3, 5- tris (2, 6- di-methyl -3- hydroxy -4-t- butyl benzyl) isocyanurate; 1, 3, 5- tris [(3, 5- di-t- butyl -4- hydroxy phenyl) propionyl oxy ethyl] isocyanurate; tris (4- t- butyl- 2, 6- di-methyl -3- hydroxy benzyl) isocyanurate; 2, 4- bis (n- octyl thio) -6- (4- hydroxy -3, 5- di- t- butyl anilino)-1, 3, 5- tri azine; tetra kis [methylene-3- (3, 5-di-t-butyl -4-hydroxy phenyl) propionate] methane; bis (3, 5-di-t- butyl -4- hydroxy benzyl ethyl phosphonate) calcium; bis (3, 5-di-t- butyl -4- hydroxy benzyl ethyl phosphonate) nickel; bis [3, 3- bis (3-t-butyl -4- hydroxy phenyl) butyric acid] glycol ester; N, N'-bis [3- (3, 5- di-t- butyl -4- hydroxy phenyl) propionyl] hydrazine; 2, 2'-oxamide bis [ethyl -3-(3, 5-di-t- butyl -4- hydroxy phenyl) propionate; bis [2-t-butyl-4-methyl -6- (3-t-butyl -5- methyl -2- hydroxy benzyl) phenyl] tere phthalate; 1, 3, 5-tri methyl -2, 4, 6-tris (3, 5- di-t- butyl -4- hydroxy benzyl) benzene; 3, 9- bis [1, 1-di-methyl -2- [β -(3-t-butyl -4- hydroxy -5- methyl phenyl) propionyl oxy] ethyl] -2,4,8,10-tetra oxa spiro [5, 5] undecane; 2, 2- bis [4-[2- (3, 5-di-t-butyl -4- hydroxy hydro cinnamoyl oxy)] ethoxy phenyl] propane and β -(3, 5-di-t-butyl-4- hydroxy phenyl) propionic acid alkyl esters such as stearyl- β -(4- hydroxy -3,5- di-t-butyl phenol) propionate, etc., can be listed. Among these, 2, 6- di-t- butyl -4- methyl phenol; stearyl -β -(4- hydroxy -3, 5-di-t-butyl phenol) propionate; 2, 2'-ethylidene bis (4, 6-di-t- butyl phenol) and tetra kis [methylene -3- (3,5-di-t-butyl-4- hydroxy phenyl) propionate] methane are suitable.

[0017]
As the organic phosphite type stabilizers, for instance; tri octyl phosphite; tri lauryl phosphite; tris tri decyl phosphite; tris iso decyl phosphite; phenyl di-iso octyl phosphite;

phenyl di-iso decyl phosphite; phenyl di (tri decyl) phosphite; di phenyl iso octyl phosphite; di-phenyl iso decyl phosphite; di phenyl tri decyl phosphite; tri phenyl phosphite; tris (nonyl phenyl) phosphite; tris (2, 4- di-t-butyl phenyl) phosphite; tris (butoxy ethyl) phosphite; tetra tri decyl -4, 4'- butylidene bis (3- methyl-6- t- butyl phenol) -di phosphite; 4, 4'-iso propylidene -di-phenol alkyl phosphite (however, the number of carbon atoms in the alkyl should be 12 to 15); 4, 4'-iso propylidene bis (2-t-butyl phenol)X di-(nonyl phenyl) phosphite; tris (biphenyl) phosphite; tetra (tri decyl) -1, 1, 3- tris (2-methyl-5-t-butyl -4- hydroxy phenyl) butane di phosphite; tris (3, 5-di-t- butyl -4- hydroxy phenyl) phosphite; hydrogenated -4, 4'-iso propylidene di-phenol poly phosphite; bis (octyl phenyl) X bis [4, 4'- butylidene bis (3- methyl -6-t- butyl phenol)]X1, 6-hexane diol di-phosphite; hexa tri decyl -1, 1, 3-tris (2-methyl -4- hydroxy -5- t- butyl phenol) di-phosphite; tris [4, 4'-iso propylidene bis (2-t-butyl phenol)] phosphite; tris (2, 3- di-stearoyl oxy iso propyl) phosphite; 9, 10- di-hydro -9- phospha phenanthrene-10-oxide; tetra kis (2, 4-di-t- butyl phenyl)- 4, 4'-bi phenylene di-phosphite; di-stearyl penta erythritol di-phosphite; di (nonyl phenyl) penta erythritol di-phosphite; phenyl X 4, 4'- iso propylidene di-phenol X penta erythritol di-phosphite; bis (2, 4-di-t- butyl phenyl) penta erythritol di-phosphite; bis (2, 6- di-t- butyl -4- methyl phenyl) penta erythritol di-phosphite; and phenyl bis phenol A - penta erythritol di-phosphite, etc., can be listed. Among these, tris (2, 4- di-t- butyl phenyl) phosphite; tris (nonyl phenyl) phosphite and tetra kis (2, 4- di-t- butyl phenyl) -4, 4'-bi phenylene di-phosphite are preferred, and especially tris (2, 4-di-t-butyl phenyl) phosphite is suitable.

[0018]

As the organic thio ether type stabilizer, it is preferred to use a di alkyl thio di propionate or the poly hydric alcohol ester of an alkyl thio propionic acid. The di alkyl thio di propionate that is used here should be preferably the di alkyl thio di propionate that has an alkyl group with 6 to 20 carbon atoms, and also, the polyhydric alcohol esters of alkyl thio propionic acids that have alkyl groups with 4 to 20 carbon atoms are preferred as the polyhydric alcohol esters of alkyl thio propionic acid. In this case, glycerin, tri methylol ethane, tri methylol propane, penta erythritol and tris hydroxy ethyl isocyanurate, etc., can be listed as examples of the polyhydric alcohols that construct polyhydric alcohol ester.

As such di alkyl thio di- propionates, for instance, di lauryl thio propionate, di- myristyl thio di-propionate and di stearyl thio di-propionate, etc., can be listed. On the other hand, as the polyhydric alcohol esters of alkyl thio propionic acid, for instance, glycerin tri butyl thio propionate, glycerin tri octyl thio propionate, glycerin tri lauryl thio propionate, glycerin tri stearyl thio propionate, tri methylol ethane tri butyl thio propionate, tri methylol ethane tri octyl thio propionate, tri methylol ethane lauryl thio propionate, tri methylol ethane stearyl thio propionate, penta erythritol tetra butyl thio propionate, penta erythritol tetra octyl thio propionate, penta erythritol tetra lauryl thio propionate, penta erythritol tetra stearyl thio propionate, etc., can be listed. Among these, di-lauryl thio di- propionate, di- stearyl thio di-propionate, penta erythritol tetra lauryl thio propionate are suitable.

[0019]

As the hindered type stabilizers, for instance, bis (2, 2, 6, 6-tetra methyl -4- piperidyl) sebacate; di-methyl succinate -1-(2-hydroxy ethyl) -4- hydroxy-2,2, 6, 6-tetra methyl piperidine poly condensed material; poly [6-(1, 1, 3, 3- tetra methyl butyl) imino-1, 3, 5- tri azine -2, 4- di-yl] [(2, 2, 6, 6- tetra methyl -4- piperidyl) imino] hexa methylene [2, 2, 6, 6- tetra methyl -4- piperidyl) imino]; tetra kis (2, 2, 6, 6- tetra methyl -4- piperidyl)- 1, 2, 3, 4- butane tetra carboxylate; 2, 2, 6, 6-tetra methyl -4- piperidyl benzoate; bis (1, 2, 6, 6- penta methyl -4- piperidyl) -2- (3, 5-di-t-butyl -4- hydroxy benzyl) -2-n- butyl maronate; bis (N-methyl-2, 2, 6, 6- tetra methyl -4- piperidyl) sebacate; 1, 1'-(1, 2- ethane di-yl) bis (3, 3, 5, 5- tetra methyl piperadinone); (mixed 2, 2, 6, 6- tetra methyl -4- piperidyl / tri decyl) -1, 2, 3, 4-butane tetra carboxylate; (mixed 1, 2, 2, 6, 6- penta methyl -4- piperidyl / tri decyl)- 1, 2, 3, 4- butane tetra carboxylate; mixed [2, 2, 6, 6- tetra methyl -4- piperidyl / β, β, β', β' - tetra methyl - 3, 9-[2, 4, 8, 10-tetra oxa spiro (5, 5) undecane] di ethyl] -1, 2, 3, 4-butane tetra carboxylate; mixed [1, 2, 2, 6, 6- penta methyl-4- piperidyl / β, β, β', β' - tetra methyl - 3, 9-[2, 4, 8, 10- tetra oxa spiro (5, 5) undecane] di ethyl]-1, 2, 3, 4- butane tetra carboxylate; N, N'-bis (3-amino propyl) ethylene diamine -2, 4- bis [N-butyl-N-(1, 2, 2, 6, 6-penta methyl -4- piperidyl) amino]-6- chloro-1, 3, 5- tri azine poly condensed material; poly [6-N-morpholyl -1, 3, 5- tri azine-2, 4- di-yl] [(2, 2, 6, 6- tetra methyl-4- piperidyl) imino] hexa methylene [(2, 2, 6, 6- tetra methyl -4- piperidyl) imide]; poly condensed material of N, N'-bis (2, 2, 6, 6- tetra methyl -4- piperidyl) hexa methylene

diamine and 1, 2- di-bromo ethane; [N-(2, 2, 6, 6- tetra methyl -4- piperidyl) -2- methyl -2-(2, 2, 6, 6- tetra methyl-4- piperidyl) imino] propion amide, etc., can be listed.

[0020]

Among these hindered amine type stabilizers, especially suitable ones are;

the poly condensed material of di-methyl succinate-1- (2-hydroxy ethyl) -4- hydroxy- 2, 2, 6, 6- tetra methyl piperidine;

poly [6-(1, 1, 3, 3- tetra methyl butyl) imino-1, 3, 5- tri azine -2, 4- di-yl] [(2, 2, 6, 6- tetra methyl -4- piperidyl) imino] hexa methylene [2, 2, 6, 6- tetra methyl -4- piperidyl) imino];

tetra kis (2, 2, 6, 6- tetra methyl -4- piperidyl)- 1, 2, 3, 4- butane tetra carboxylate;

bis (1, 2, 6, 6- penta methyl -4- piperidyl) -2- (3, 5-di-t-butyl -4- hydroxy benzyl) -2-n- butyl maronate;

1, 1'-(1, 2- ethane di-yl) bis (3, 3, 5, 5- tetra methyl piperadinone);

(mixed 2, 2, 6, 6- tetra methyl -4- piperidyl / tri decyl) -1, 2, 3, 4-butane tetra carboxylate;

(mixed 1, 2, 2, 6, 6- penta methyl -4- piperidyl / tri decyl)- 1, 2, 3, 4- butane tetra carboxylate;

mixed [2, 2, 6, 6- tetra methyl -4- piperidyl / β, β, β', β' - tetra methyl - 3, 9-[2, 4, 8, 10-tetra oxa spiro (5, 5) undecane] di ethyl] -1, 2, 3, 4-butane tetra carboxylate;

mixed [1, 2, 2, 6, 6- penta methyl-4- piperidyl / β, β, β', β' - tetra methyl - 3, 9-[2, 4, 8, 10-tetra oxa spiro (5, 5) undecane] di ethyl]-1, 2, 3, 4- butane tetra carboxylate;

N, N'-bis (3-amino propyl) ethylene diamine -2, 4- bis [N-butyl-N-(1, 2, 2, 6, 6-penta methyl -4- piperidyl) amino]-6- chloro-1, 3, 5- tri azine poly condensed material;

poly [6-N-morpholyl -1, 3, 5- tri azine-2, 4- di-yl] [(2, 2, 6, 6- tetra methyl-4- piperidyl) imino] hexa methylene [(2, 2, 6, 6- tetra methyl -4- piperidyl) imide];

poly condensed material of N, N'-bis (2, 2, 6, 6- tetra methyl -4- piperidyl) hexa methylene diamine and 1, 2- di-bromo ethane; and

[N-(2, 2, 6, 6- tetra methyl -4- piperidyl) -2- methyl -2- (2, 2, 6, 6- tetra methyl-4- piperidyl) imino] propion amide.

[0021]

If desired, additives can be blended into the modified poly ethylenic resin of this invention

that is obtained like this in the range in which the objective of this invention will not be impaired, for instance a neutralizer (metal soap, hydrotalcite), a weather resistance agent and stabilizer, a heat resistance agent and stabilizer, an anti static agent, a slip preventon agent, an anti blocking agent, an anti turbidity agent, lubricants, pigments, dyes, nucleation agents, plasticizers, an aging prevention agent, etc., can be added. The inflation film of this invention uses the above mentioned modified poly ethylenic resin as the base material, and the inflation forming method is not particularly limited, and the already known methods until now, can be used, however, the forming conditions should be preferably a temperature of 160 to 340 °C, and the blow up ratio should be in the range of 1.1 ~ 6.0. If the temperature is lower than 160 °C, the poly ethylenic resin sometimes does not melt sufficiently, and when it exceeds 340 °C, the resin deteriorates, and the quality of the film sometimes decreases. On the other hand, when the blow up ratio is less than 1.1, or exceeds 6.0, it becomes difficult to obtain a high quality film with good balance in the lengthwise and transverse directions. The thickness of the inflation film obtained like this should be normally in the range of 5 to 100 μm, preferably 10 to 60 μm.

[0022]

[Actual Examples]

Next, this invention will be explained in more detail referring to actual examples, however, this invention will not be limited to these examples. The physical properties of the resin and the oxygen concentrations were measured by the following methods.

(1) Physical properties of the resin

(i) Density

This was measured according to JIS K7112.

(ii) MFR

According to JIS K7210, this was measured at 190 °C under a load of 21.18 N, or 49 N.

(iii) tan δ

The sample used for measuring the tan δ was prepared as follows. In the case of

16

measuring the tan δ of the poly ethylenic resin before modification, the powder before modification was melt-pressed at 190 °C for 3 minutes, and a 1 mm thick disc was made, and this was used as the sample for measurement. In the case of measuring the tan δ after modification, the pellets after modification were melt-pressed at 190 °C for 3 minutes, and a 1 mm thick disc was made, and this was used as the sample for measurement. The disc obtained by press-forming was put between a cone and a flat board, and a dynamic distortion was induced at a temperature of 190 °C and 15 % distortion, and the storage modulus G' and the loss modulus G@ with an angular frequency of 1.5×10^{-2} rad / sec, were measured, and the loss tangent, tan δ, was obtained by the following equation. An ARES made by Leometric? (*spelling uncertain, Translator*) Co. was used for measurement.

tan δ = G" / G'

(iv) YI (Yellow Index)
Using the pellets from the modified poly ethylenic resin, YI was measured according to JIS K7103.

[0023]
(2) Oxygen concentration
The oxygen concentration was measured by an oxygen concentration detector. The physical properties of the film were measured by the following methods.

(3) Physical properties of film
(i) Impact strength
After inflation forming, the impact strength of the inflation film was measured using an film impact tester (made by Toyo Seiki Seisakusho K.K.) at the JIS standard temperature state class 2 (23 ∀ 2 °C) and standard humidity state class 2 (50 ∀ 5 % RH), after maintaining the state adjusting time for 24 hours or more. The hammer force was set 294 NX cm.

(ii) Fish eyes (from now on this will be indicated as FE)

FE are round lumps or streaks that appear on the film surface. The number of FE in 1000 cm^2 was visually counted by holding the film up to a flourescent light.

(iii) Forming stability of film

If the film did not break under the following inflation forming conditions, the bubble stability was considered to be good (±) and if it was broken, it was X (bad).

Extruder : Plako? (*spelling uncertain, Translator*) NLM (500 mm diameter)

Die type : Plako? SG-11-100F6 special

Lip part diameter : 100 mm

Gap : 1.2 mm

Land length : 20 mm

Spiral part outer diameter : 110 mm, Number of lines : 6

Discharge flow rate : 68 kg / hr,

Take up speed : 51 m / min,

Lay flat width of film : 500 mm

Thickness of film : 25 μm, Set temperature : 200 °C, Blow up ratio : 3.4

(iv) Deviation of thickness in film

The film thickness was continuously measured in the circumferential direction, and the standard deviation of this data was obtained and it was used as the scale for thickness unevenness.

[0024]

Example 1

Using a continuous slurry two- stage polymerization device, ethylene only was polymerized using a titanium type catalyst in the earlier stage, and the polymer of which the MFR_2 = 950 g / 10 min at 190 °C with a load of 21.18 N, and a density of 982 kg / m^3 was obtained. Next, it was transferred to the second stage polymerization device, and ethylene and 1-butene were co-polymerized using a titanium type catalyst, again in the presence of a polymerization hexane solution. The hexane suspended liquid of the

obtained ethylenic co-polymer was separated from the liquid by centrifugation at 60 °C, and the obtained wet powder cake was continuously dried in a powder drier at 100 °C with a residence time of 1 hour. After drying, the poly ethylenic resin powder I was taken out from the device, and the density was measured. It was found to be 949 kg / m^3. The MFR$_5$ at 190 °C with a load of 49 N was 0.20 g / 10 min, and the tan δ = 1.27. The ratio of the polymerization amount in the first stage and the second stage was set at 53 : 47 as the weight ratio. These results are shown in Table 1.

[0025]

1000 ppm of Irgahos? (*spelling uncertain - may be a typo of Irganox, Translator*) 168, 500 ppm of Irganox 1000, and 3000 ppm of calcium stearate were blended into the obtained powder I of poly ethylenic resin inside the system without contacting it with air at all, and continuously it was fed into the hopper of a tandem type biaxial kneading extruder. As can be seen in Figure 1, the first step of the extruder is a biaxial kneader CIM-50 (made by Nihon Seiko K.K.), and the second stage is a single axis extruder P65-13SW (made by Nihon Seiko K.K.), and the oxygen containing- gas was introduced into the supply hopper in the first step. Melt- forming was performed using this kneader, and after strand cutting, the pellet- shaped modified poly ethylenic resin was obtained. The kneading conditions are shown in Table 1-2. Figure 1 is the outline of the extruder that was used in this Example. Inflation forming was performed by using the obtained modified poly ethylenic resin under the following conditions.

[0026]

Inflation forming conditions

Extruder : Plako? NLM (50 mm diameter)

Die type : Plako? SG-11-100F6 special

Lip part outer diameter : 100 mm diameter, Gap : 1.2 mm, Land length: 20 mm,

Spiral part outer diameter : 110 mm diameter, Number of lines : 6,

Discharge flow rate : 56 kg / hr,

Take up speed : 42 m / min,

Lay flat width of film : 500 mm

Thickness of film : 20 μm, Set temperature : 200 °C, Blow up ratio : 3.4

The physical properties of the modified poly ethylenic resin and the evaluation results of the film properties are shown in Table 1-3.

[0027]

Example 2

Using poly ethylenic resins II and III shown in Table 1-1, the pellet form, modified poly ethylenic resin was obtained the same as in Example 1 under the conditions 1 shown in Table 1-2. The results are shown in table 2.

[0028]

[Table 1]

Table 1-1

		Poly ethylenic resin before modification		
		I	II	III
Compo sition	Density (kg / m^3)	949	952	956
	MFR$_5$? (g / 10 min)	0.20	0.18	0.24
	tan δ	1.27	1.39	1.22
(A)	Resin	Ethylene homo polymer	Ethylene homo polymer	Ethylene homo polymer
	MFR$_2$? (g / 10 min)	950	960	1020
	Density (kg / m^3)	982	982	982
(B)	Resin	Ethylene / 1-butene co-polymer	Ethylene / 1-butene co-polymer	Ethylene / 1-butene co-polymer
	Number of carbon atoms in α- olefin	4	4	4
A : B (weight ratio)		53 : 47	54 : 46	52 : 48

[0029]

[Table 2]

Table 1-2

Kneading conditions No. of Example 1		1	2	3	4
CIM	Discharge rate (kg / hr)	50	50	50	50
	Rotor rotation (rpm)	1450	1450	1450	1450
	Slot opening (mm)	2.0	2.0	2.0	2.0
	Chamber conditions (water bath: °C)	50	50	50	50
	Position of adding oxygen- containing gas	Hopper	Hopper	Hopper	Hopper
	Concentration of oxygen (vol %)	1.0	3.0	5.0	21.0
EXT	Number of rotations of extruder (rpm)	80	80	80	80
	Cylinder set temperature (°C)	208	208	208	208

[0030]

[Table 3]

Table 1-3

Experiment No. of Example 1			1-1	1-2	1-3	1-4
Un-modified poly ethylenic resin No.			I	I	I	I
Kneading	Specific energy (kW Xh/ kg)	CIM	0.23	0.23	0.22	0.20
		EXT	0.09	0.09	0.08	0.07
Modified poly ethylenic resin	tan δ		1.85	1.67	2.03	2.24
	Δ tan δ (%)		46	31	60	76
	YI		-1.0	- 0.4	0.1	2.2
Physical properties of film	Impact strength (kJ? / m)		37	36	31	30
	Deviation in thickness (μm)		1.0	1.0	1.0	1.0
	FE (how many)		31	32	36	42
	Forming ability		±	±	±	±

[0031]

[Table 4]

Table 2

Experiment No. of Example 2			2-1	2-2
Un-modified poly ethylenic resin No.			II	III
Kneading	Specific energy (kW Xh/ kg)	CIM	0.25	0.21
		EXT	0.11	0.07
Modified poly ethylenic resin	tan δ		2.01	1.79
	Δ tan δ (%)		45	47
	YI		- 1.5	- 0.8
Physical properties of film	Impact strength (kJ? / m)		35	33
	Deviation in thickness (μm)		1.0	1.0
	FE (how many)		24	18
	Forming ability		±	±

[0032]

Example 3

900 ppm of Irugahos? 168, 600 ppm of Irganox 1010, and 2800 ppm of calcium stearate were blended into the powder I that was polymerized the same as that in Example 1 inside the system without any contact with air, and then it was placed in a 200 L container made out of SUS that had been purged with nitrogen. The SUS container in which the powder was placed, was connected to the extruder feeder, and after the inside of the feeder was completely purged with nitrogen, the gate was opened and powder was supplied into the feeder while supplying pressurized nitrogen (See Figure 2 (a)). The biaxial extruder that was used was a same rotational direction biaxial extruder TEX30HSS-32.5 PW-2V (made by Nihon Seiko K. K.). As can be seen in Table 3-1, the melt-kneading was performed changing the position of the oxygen addition and changing the added concentrations, and after the strands were cut, the pellet- like modified poly ethylenic resin was obtained. Here, the oxygen- containing gas was introduced at the hopper chute (see Figure 2 (a)) or at the second cylinder (see Figure 2 (b)). The results are shown in Table 3-2. Figure 2 (a) is an outline of the extruder that was used in this actual example, and Figure 2 (b) is the enlarged view of the extruder part shown in Figure 2 (a). In the figure, 1 indicates the container made out of SUS. 2 is the feeder, and 3 is the chute.

[0033]

[Table 5]

Table 3-1

No.	Discharge rate (kg / h)	Rotation (min^{-1})	Cylinder set temperature ($^\circ$C)	Place where oxygen was added	Oxygen concentration (vol %)
Kneading conditions of Example 3					
3-1	10	280	200	Second cylinder	2
3-2	10	280	200	Second cylinder	5
3-3	10	280	200	Second cylinder	10
3-4	10	280	200	Hopper chute	2
3-5	10	280	200	Hopper chute	5
3-6	10	280	200	Hopper chute	21

[0034]

[Table 6]

Table 1-3

Experiment No. of Example 3		3-1	3-2	3-3	3-4	3-5	3-6
Un-modified poly ethylenic resin No.		I	I	I	I	I	I
Modified poly ethylenic resin	tan δ	1.57	1.71	2.01	1.54	1.61	2.30
	Δ tan δ (%)	24	35	58	21	26	81
	YI	- 1.1	- 0.5	1.2	- 0.9	- 0.3	2.4
Physical properties of film	Impact strength (kJ? / m)	37	35	31	37	36	30
	Deviation in thickness (μm)	1.0	1.0	1.0	1.0	1.0	1.0
	FE (how many)	32	37	34	34	36	44
	44Forming ability	±	±	±	±	±	±

[0035]

[Effect of the Invention]

According to this invention, the poly ethylenic resin that can be used to produce the inflation film of which the bubble stability during the inflation forming time is good, and also which has excellent balance in the physical properties such as good impact strength and less deviation in the thickness, and also which has less fish eyes, can be produced efficiently.

[Simple Explanation of Figures]
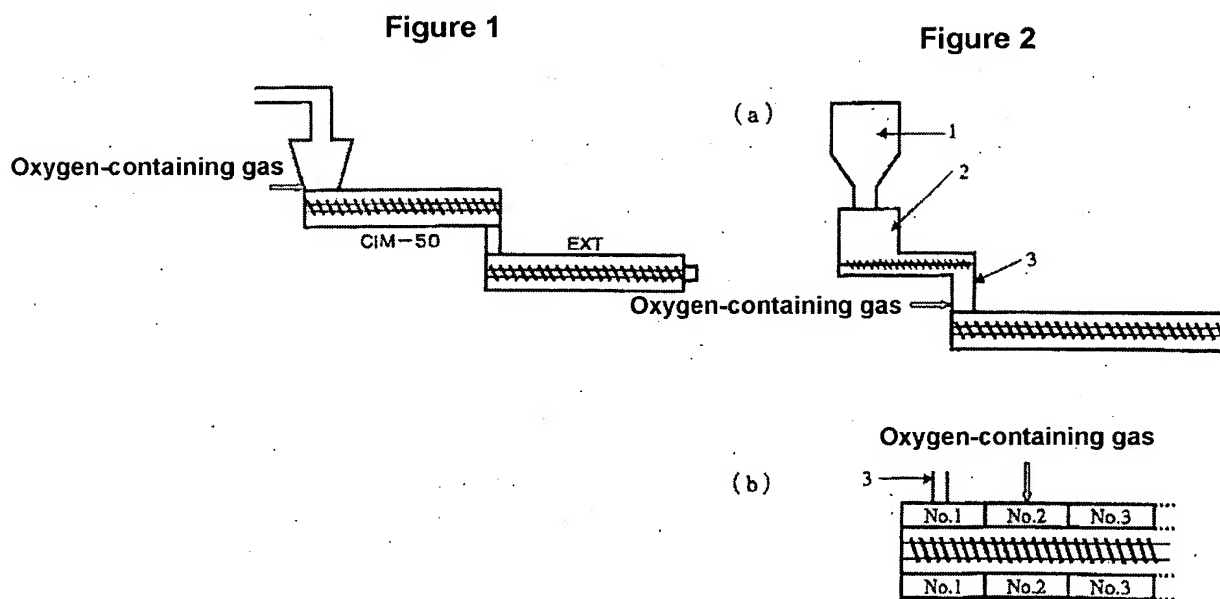
[Figure 1]

This is the outline of the extruder that was used in Examples 1 and 2.

[Figure 2]

These are the outlines of the extruder that was used in Example 3 (a), and an enlarged view of the extruder part (b).

[Explanation of Marks]

1   Container made by SUS

2   Feeder

3   Chute

Figure 1

Oxygen-containing gas

CIM—50   EXT

Figure 2

(a)

Oxygen-containing gas

(b)

Oxygen-containing gas

No.1	No.2	No.3

No.1	No.2	No.3

Continued from the front page.

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The remaining page of Japanese text contains corrections; these corrections have been included in the translation - Translator

Axtell, Carol (CA)

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